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Evaluation of Polyurethane Foam Cartridges for Measurement of Polynuclear Aromatic Hydrocarbons in Air

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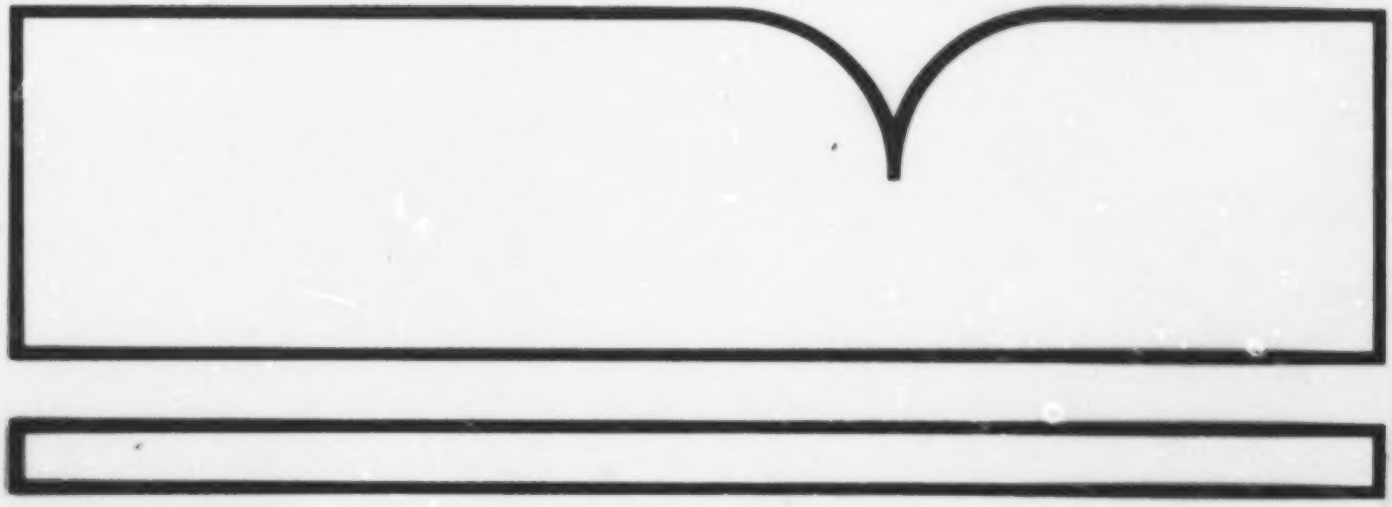

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EVALUATION OF POLYURETHANE FOAM CARTRIDGES FOR MEASUREMENT OF POLYNUCLEAR AROMATIC HYDROCARBONS IN AIR

by

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16. ABSTRACT The objective of this project was to evaluate polyurethane foam (PUF) cartridges as collection media for quantification of vapor phase polynuclear aromatic hydrocarbons (PAHs) in air. Two cleanup methods for PUF cartridges -- compression rinsing and combined compression rinsing and Soxhlet extraction -- have been evaluated. Both methods successfully remove interfering material and background PAHs from the PUF. The compression rinsing method is recommended because it is easier, faster, and cheaper.

Two procedures for extraction of PAHs from the PUF matrix, Soxhlet extraction and compression rinsing, were compared. These sample extracts were analyzed by on-column injection, electron impact gas chromatography/mass spectrometry (EI GC/MS) to determine PAHs. The results showed that compression rinsing is comparable to conventional Soxhlet extraction, and that both methods successfully remove PAHs from the PUF cartridges. The compression rinsing method was then used in the stability study.

The stability study was carried out to determine the stability of PAHs adsorbed on PUF cartridges as a function of storage time between collection and extraction. The results indicated that the levels of the spiked perdeuterated benzo(a)pyrene decreased significantly during storage. The rate of decrease was much faster when the PUF cartridges were stored in light. Other PAH levels were not adversely influenced by the storage time.

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FOREWORD

Measurement and monitoring research efforts are designated to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for assessment of environmental monitoring technology and systems, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of human exposure to toxic organic compounds is an area of increasing significance to EPA. The evaluation of polyurethane foam cartridges for polynuclear aromatic hydrocarbon measurements provides important information that can be applied to the measurement of the extent of human exposure to the polynuclear aromatic compounds.

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ABSTRACT

The objective of this project was to evaluate polyurethane foam (PUF) cartridges as collection media for quantification of vapor phase polynuclear aromatic hydrocarbons (PAHs) in air.

Two cleanup methods for PUF cartridges -- compression rinsing and combined compression rinsing and Soxhlet extraction -- have been evaluated. Both methods successfully remove interfering material and background PAHs from the PUF. The compression rinsing method is recommended because it is easier, faster, and cheaper.

Two procedures for extraction of PAHs from the PUF matrix, Soxhlet extraction and compression rinsing, were compared. Modified EPA medium volume samplers having quartz fiber filters to collect particles and PUF cartridges to trap vapors were used. Prior to sampling, known quantities of perdeuterated PAHs were spiked into each cleaned PUF cartridge. Eight samplers were operated outdoors in parallel for 24 hours. After sampling, four PUF samples were Soxhlet-extracted with 10 percent ether/hexane and the other four PUF samples were extracted by alternate compression and decompression fifty times in the same solvent. These sample extracts were analyzed by on-column injection, electron impact gas chromatography/mass spectrometry (EI GC/MS) to determine PAHs. The results showed that compression rinsing is comparable to conventional Soxhlet extraction, and that both methods successfully remove PAHs from the PUF cartridges. The compression rinsing method was then used in the stability study.

The stability study was carried out to determine the stability of PAHs adsorbed on PUF cartridges as a function of storage time between collection and extraction. Two sets of PUF samples were collected for this study. The first set of samples was stored in the presence of light, and the second set of samples was kept in the dark. The storage temperature for both sets of samples was approximately 20°C. The samples were stored for one, ten, twenty, or thirty days and then extracted with 10 percent ether/hexane. Sample extracts were analyzed by EI GC/MS. The levels of perdeuterated benzo(a)pyrene decreased significantly during storage. The rate of decrease was much faster when the PUF cartridges were stored in light. Other PAH levels were not adversely influenced by the storage time.

Selected sample extracts obtained from the pilot study of previous work (Task 35) were solvent exchanged into dimethylsulfoxide at eight different concentration levels. These samples were packed in dry ice and sent to EPA, HERL/ERC for microbioassay analysis.

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LIST OF ABBREVIATIONS

BaP	benzo(a)pyrene
CI	chemical ionization
D_o-PAH	native polynuclear aromatic hydrocarbons
DMSO	dimethyl sulfoxide
D_n-PAH	perdeuterated polynuclear aromatic hydrocarbons
EI	electron impact
GC/MS	gas chromatography/mass spectrometry
PAC	polynuclear aromatic compounds
PAH	polynuclear aromatic hydrocarbons
PCB	polychlorinated biphenyls
RIC	recontructed ion chromatogram
PUF	polyurethane foam

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SECTION 1

INTRODUCTION

Polynuclear aromatic compounds have been extensively studied and have received increased attention in studies of air pollution in recent years because some of these compounds are highly carcinogenic or mutagenic. To understand the extent of human exposure to polynuclear aromatic compounds, reliable sampling and analytical methodology must be established for monitoring the concentrations of these compounds in air. In general, the analytical methodology is well developed, but the sampling procedures can often reduce the validity of analytical results. Several studies (1-4) have shown that the three- to four-ring polynuclear aromatic hydrocarbons (PAH) in air may be mainly in the vapor phase and are not retained by filters because of volatilization. A wide variety of adsorbents such as Tenax-GC, XAD-2 resin and polyurethane foam (PUF) has been used to sample organic vapors (5). The PUF cartridge is easy to handle in the field and has good airflow characteristics; it has been successfully used for collection of pesticide and polychlorinated biphenyl (PCB) vapors (6).

Recently, Battelle conducted a study (7) to collect ambient and indoor air PAH using a sampler with a quartz fiber filter and a PUF back-up trap. It was observed that the PUF cartridges changed from a pale white to a light yellow color over a one week storage period. It is not known whether this color change during storage is associated with any change in the PUF cartridge's ability to retain PAHs. In a large scale air monitoring program, placement of the samplers in the field and the return of filters and traps after air collection to analytical laboratories may involve several weeks. Therefore it is necessary to conduct a study to assess the stability of PAHs adsorbed on the PUF cartridges during storage.

The objective of this project was to evaluate PUF cartridges for collection and subsequent analysis of vapor phase PAH in air. Two studies were performed:

(a) Extraction study to evaluate two extraction procedures, Soxhlet extraction and compression rinsing, for removal of PAH from the PUF matrix.

(b) Stability study to determine the stability of PUF traps by examining the measured PAH concentration as a function of storage time between collection and extraction.

The sample extracts were analyzed by electron impact gas chromatography/mass spectrometry (EI GC/MS) to determine both native PAHs and spiked perdeuterated PAHs.

In addition, sample extracts obtained from the range-finding study done under a previous work assignment [Task 35 (7)] were solvent exchanged into dimethyl sulfoxide at eight different levels and sent to EPA, HERL/ERC for microbioassay.

SECTION 2

CONCLUSIONS

Two PUF cleanup methods, compression rinsing and combined compression rinsing and Soxhlet extraction, have been evaluated for their ability to remove interfering material and background PAHs from PUF cartridges. The results showed that the compression-only technique is comparable to the combined compression and Soxhlet extraction method. Thus the compression method is recommended for use in the future for time and cost savings.

The results of the extraction study indicated that levels of both native and perdeuterated PAHs found in the PUF cartridges were similar using either Soxhlet extraction or compression rinsing. It has been demonstrated that both methods can successfully remove PAHs from the PUF cartridges. Since significant time and cost savings can be achieved by using compression rinsing, this method was used in the stability study.

Generally, good recoveries for the spiked perdeuterated PAHs were obtained for PUF samples extracted immediately after collection, with the exception of D_8-naphthalene. This finding demonstrated that PUF cartridges cannot quantitatively retain volatile two-ring PAHs under the sampling conditions employed. Greater loss of volatile components would be expected at higher sampling temperatures. It should be noted that cyclopenta(c,d)pyrene and higher molecular weight ($\geq$252) PAHs were not detected in the PUF samples. 1-Nitropyrene was also not found in the PUF samples.

The stabilities of PAHs adsorbed on PUF cartridges during storage with and without light were investigated. The results indicated that levels of BaP decreased significantly during storage. The rate of decrease was much faster when PUF cartridges were stored in the

presence of light. The levels of the remaining PAHs were not significantly influenced by the storage time.

SECTION 3

RECOMMENDATIONS

Both XAD-2 resin and polyurethane foam (PUF) are commonly used to collect PAH vapors in ambient air sampling (8). A comparative study is recommended to evaluate the flow characteristics and the collection efficiency for PAH vapors by using these two adsorbents (XAD-2 and PUF) as backup traps in ambient air sampling. Recently, several research groups indicated that extracts of clean PUF plugs show mutagenic activity and interfere with bioassay results (9). Therefore, bioassay analysis is recommended for samples collected from these two adsorbents. The bioassay results can provide information as to whether PUF plugs or XAD-2 resin would interfere with bioassay. To characterize and to compare these two adsorbents thoroughly, studies are also recommended to determine the stability of PAHs captured on XAD-2 resin as a function of time.

In this study, quartz fiber filters were used to collect air particulate matter. However, there are other types of filters which can be considered for collection of particles. Very few studies have been conducted to evaluate filter material for collection of particle-bound PAHs. Lee's group (10) has evaluated various candidate filter materials such as glass fiber, quartz fiber, microglass fiber with Teflon binder and Teflon membrane filters. Experiments were performed by liquid-spiking BaP onto filters to determine the recoveries. However, the liquid-spiking BaP does not represent the native adsorption state of BaP in ambient air sampling. Therefore, it is recommended that an evaluation study be conducted to compare different types of filters such as quartz fiber, glass fiber, and Teflon-coated filters for collection of PAHs in ambient air sampling. Several important filter

characteristics such as flow characteristics and collection efficiency should be addressed.

Studies to determine stabilities for different types of filters and to determine the effects of storage time on PAH samples collected on different types of filters are also recommended.

SECTION 4

EXPERIMENTAL PROCEDURES

SAMPLING METHODOLOGY

In both the extraction and stability studies, eight EPA medium volume samplers using General Metals bypass motors in place of the original high volume blower motors were employed. Quartz fiber filters were used to collect particulate matter and polyurethane foam (PUF) cartridges were used to collect vapors. Samplers were located outside Battelle away from any exhaust openings or heavy traffic. Two sets of four samplers were placed in parallel approximately two feet apart. In each set, the samplers were placed about one foot apart. A five foot long exhaust hose was attached to each sampler leading away from the sampler inlet to avoid recirculating the exhaust air to the filter and the PUF trap. Prior to sampling, the sampler pump was turned on and the flow rate was measured by means of a calibration head and a U-tube manometer. Adjustments were made with a control and a bypass valve to obtain a flow rate of 8 cfm. All the clean PUF traps were spiked with 100 µL of a methylene chloride solution containing nominally 50 µg/mL of each of five perdeuterated PAHs. Then the spiked PUF cartridges and the clean filters were placed in the sampling heads. Air was sampled for 24 hours. After 24 hours of sampling, a final flow check was conducted on each sampler, and all PUF cartridges and filters were processed for transport to the laboratory for analysis.

CHEMICAL ANALYSIS METHODOLOGY

Polyurethane Foam Cartridge Cleanup Methods

Two methods for cleanup of PUF cartridges were examined: compression rinsing followed by Soxhlet extraction, and compression

rinsing only. Two PUF plugs were cleaned by compression rinsing, which consisted of placing a PUF plug in a beaker containing 800 mL of toluene, compressing it and allowing it to expand 50 times, using the base of a 250 mL graduate cylinder to compress the foam. This process was repeated using acetone. The PUF cartridges were then Soxhlet-extracted with acetone for 16 hours and dried in a vacuum oven using water aspirator vacuum at room temperature. Another two PUF cartridges were cleaned by compression rinsing and drying as above, but the Soxhlet extraction with acetone was omitted. After drying, the four cleaned PUF cartridges were Soxhlet-extracted with 10 percent ether in hexane for 16 hours. The extracts were concentrated to 1 mL and the internal standard, 9-phenylanthracene, was added to give a final concentration of 5 µg/mL. These PUF extracts were analyzed by EI GC/MS to determine the background levels of PAHs found in the cleaned PUF cartridges.

Polyurethane foam cartridges to be used in the recovery study, the extraction methods comparison, and the storage stability study were cleaned by compression rinsing with toluene and acetone followed by Soxhlet extraction with acetone and drying as above. Following cleanup, the PUF cartridges were wrapped with hexane-rinsed aluminum foil and placed in 32-ounce jars closed with Teflon-lined caps until they were used. Typically, all the PUF cartridges were cleaned within 24 hours prior to sampling.

Method of Preparation of Standard Solutions

The spiking stock solution containing five D_n-PAHs was prepared in methylene chloride and was stored in a 100 mL volumetric flask at a nominal concentration level of 50 µg/mL for each compound. The actual concentrations of this spiking solution are listed in Table 4.1. Four 1 mL aliquots of the spiking stock solution were transferred into four 2 mL GC vials for field use. Prior to sampling, exactly 100 µL of the spiking solution was withdrawn into a 100 µL syringe, and the spike was injected approximately 1 inch deep into the cleaned PUF cartridge.

Another stock solution containing selected native PAHs was prepared at a nominal concentration of 100 µg/mL per compound. The

TABLE 4.1. LEVEL OF DEUTERATED PAHs IN THE SPIKING STOCK SOLUTION

Compound	Concentration of Standard, µg/mL
D_8-Naphthalene	55
D_{10}-Phenanthrene	51
D_{10}-Pyrene	56
D_{12}-Chrysene	48
D_{12}-Benzo(a)pyrene	58

concentrations in this stock solution are given in Table 4.2. This stock solution was used to prepare nominal 1, 5 and 10 µg/mL standard solutions which also contained the spiked D_n-PAHs and the internal standard, 9-phenylanthracene, at a constant concentration of 5 µg/mL.

TABLE 4.2. LEVEL OF NON-DEUTERATED PAHs IN THE STOCK STANDARD SOLUTION

Compound	Concentration of Standard, µg/mL
Phenanthrene	119
Fluoranthene	124
Pyrene	106
Benz(a)anthracene	102
Benzo(e)pyrene	113
Benzo(a)pyrene	105
Benzo(g,h,i)perylene	93
Coronene	109
1-Nitropyrene	103

Method of Extraction Study

Eight PUF and filter samples were collected in the extraction study. The filter samples were wrapped with aluminum foil, stored at room temperature, and were not analyzed in this program. Four PUF samples were Soxhlet-extracted with 800 mL 10 percent ether/hexane for 16 hours. After extraction, the sample extracts were concentrated to 1 mL and transferred into 2 mL sample vials.

Another four PUF samples were extracted with 800 mL of 10 percent ether/hexane using the compression technique. The PUF plug was placed in a beaker containing 800 mL of 10 percent ether/hexane and was compressed fifty times using the base of a 250 mL graduate cylinder. Then the sample extract was evaporated to 1 mL and transferred into a 2 mL sample vial. Prior to GC/MS analysis, the internal standard, 9-phenylanthracene, was added to all the sample extracts to give a constant concentration of 5 µg/mL. The levels of D_0-PAHs and D_n-PAHs in these PUF samples were determined using EI GC/MS.

Method of Stability Study

Two sets of sampling were conducted in the stability study. The first set of sampling employed eight EPA medium volume samplers, but the motors of two samplers burned out during sampling. Because the total volumes sampled for these two samples were not known, only six PUF samples were available for the study. The sampling was repeated one week later to obtain the second set of samples. After 24 hour sampling, eight PUF samples were collected for the stability study.

Neither the first nor the second set of filter samples were analyzed in this study. Only PUF samples were used in the stability study; these were stored under different conditions. The first set of PUF samples was stored in the presence of white fluorescent light (room lights) at room temperature; the wavelengths and intensities of the light were not measured. The second set of PUF samples was wrapped individually with aluminum foil and stored in the dark at room temperature. Two PUF samples from each set were extracted with 10 percent ether/hexane usingthe compression technique immediately after

sampling. The remaining PUF samples were stored either in the light or in the dark for ten-, twenty- or thirty-day intervals and extracted with 10 percent ether/hexane. Sample extracts were concentrated to 1 mL for GC/MS analysis. The internal standard, 9-phenylanthracene, was added to all sample extracts at a level of 5 µg/mL prior to GC/MS analysis.

Method of Analysis by Gas Chromatography/ Mass Spectrometry (GC/MS)

Electron impact gas chromatography/mass spectrometry (EI GC/MS) in the full mass scan mode was employed to determine D_0-PAHs and the spiked D_n-PAHs in the PUF samples. The instrumental conditions used are listed in Table 4.3. A Finnigan Model 4500 quadrupole mass spectrometer equipped with an EI/CI source was employed. The mass ranges were scanned from 50 amu to 450 amu at 1 sec scan rate. The ion source temperature was held at 160°C and the electron multiplier was operated at approximately 10^5 gain.

Gas chromatography employed an Ultra #2 fused silica capillary column (50 m x 0.31 mm I.D., 0.17 µm film thickness, Hewlett-Packard Co.) and methane carrier gas. The GC column interfaced directly to the MS ion source. With on-column injection, the sample was injected at 45°C to prevent thermal degradation of thermally labile compounds such as 1-nitropyrene. The GC column temperature was held at 45°C for 2 min, programmed rapidly to 100°C in 5 min, and then programmed from 100°C to 320°C at 6°C/min.

The standard solutions and sample extracts were analyzed by EI GC/MS. Identification of the PAH compounds in the sample extracts was based on the correct mass spectrum and the correct retention time relative to the internal standard as determined from the standard analyses. From the standard analyses, the response factor for each compound relative to the internal standard was calculated over the calibration range. The following equation shows the factors on which quantification was based:

$$C_x = \frac{A_x \times C_{is} \times F_x}{A_{is} \times R_f}$$

TABLE 4.3. GC AND MS OPERATING CONDITIONS

Chromatography	
Column:	HP Ultra #2 crosslinked 5% phenyl methyl silicone 50 m x 0.31 mm, 0.17 μm film thickness
Carrier Gas:	CH_4 flow rate at 60 cm^3/sec at 250°C
Injection Volume:	1 μL
Injection Mode:	On-column at 45°C
Temperature Program	
Initial Column Temperature:	45°C
Initial Hold Time:	2 minutes
Program:	45° to 100°C in 5 min, then 100°C (5 min) to 320°C at 6°C/min
Final Hold Time:	10 minutes
Mass Spectrometer	
Instrument:	Finnigan 4500 GC/MS
Ionization:	Electron impact at 70 eV
Emission Current:	0.3 ma
Scan:	50-450 amu; 1.0 sec/scan
Preamplifier:	10^{-8} amp/volt

where

C_x = Total µg of a target compound in the extract
A_x = Molecular ion area of a target compound
C_{is} = Concentration of the internal standard
A_{is} = Molecular ion area of the internal standard
R_f = Response factor of a target compound
F_v = Final volume of sample extract.

Method of Preparation of Sample Extracts for Microbioassay

Since the microbioassay is conducted directly in the vials containing the sample extracts, the vials must be clean and free of chemical or biological interference. Therefore, prior to solvent exchange, the vials to be used for shipping and bioassay were placed in a 500°C oven heated overnight, and the screw caps were Soxhlet-extracted with methanol for 16 hours. Sample extracts from the pilot study of the previous work (7) were diluted with methylene chloride to a concentration of 3.77 mg/mL. A one mL aliquot was removed from each sample extract for further dilution to 1 mg/ml and the remaining portions were stored in the dark at -70°C. The diluted extracts (1 mg/mL) were then divided into 16 sample vials at eight different levels of mass in duplicate. The conditions for sample division are summarized in Table 4.4. The sample extracts were evaporated to near dryness under a gentle nitrogen stream and 2 µL of dimethylsulfoxide (DMSO) was added to each sample. The DMSO samples were mixed with a Vortex mixer and evaporated under nitrogen for additional five minutes. Then the sample vials were sealed with screw caps and immediately stored under dry ice. The samples were packed in dry ice and sent to EPA at HERL/ERC for microbioassay with and without metabolic activation (+S9,-S9).

TABLE 4.4. MASS DISTRIBUTION OF SAMPLE EXTRACTS FOR MICROBIOASSAY

Level of Mass in Sample Vial, µg	Size of Syringe Used, µL	Number of Vials	Amount of DMSO added, µL
1000	1000	2	2
500	500	2	2
200	250	2	2
100	100	2	2
50	50	2	2
20	25	2	2
10	10	2	2
5	10	2	2

SECTION 5

RESULTS AND DISCUSSION

The results of cleaning the PUF cartridges by two different methods are summarized in Table 5.1. Only small quantities of naphthalene were found in the PUF cartridges cleaned by either the compression method or the combined compression and Soxhlet extraction method. However, as shown in Figures 1 and 2, an unknown impurity peak which is about 90 percent of the total chromatographic peaks was detected in the clean PUF cartridges after both of these two different cleaning methods.

The results of the extraction study are presented in Table 5.2 and 5.3. As shown in Table 5.2, generally good recoveries (>85 percent) were obtained for spiked D_n-PAHs with the exception of D_8-naphthalene using either the Soxhlet extraction or the compression method. The loss of D_8-naphthalene was anticipated since this compound is highly volatile. The sampling temperature during this experiment was 0°C to 10°C. Even greater losses of this volatile compound can be expected at higher sampling temperatures.

As shown in Table 5.3, the levels of native PAHs found in the PUF cartridges were very similar using these two methods. The levels of PAHs found in the PUF cartridges, expressed as ng per cubic meter of air sampled, ranged from 0.10 ng/m^3 to 29.39 ng/m^3 and 0.17 ng/m^3 to 28.41 ng/m^3 using the Soxhlet-extraction and the compression methods, respectively. These data demonstrate that the compression technique is comparable to Soxhlet-extraction in removing PAHs from the PUF cartridges. Since significant time and cost savings can be achieved by using the compression method, this method was used in the stability study.

Only volatile and semi-volatile PAHs were found in the PUF cartridges. Higher molecular weight PAHs($\geq$252), such as benzo(a)pyrene and coronene, and 1-nitropyrene were not detected in the PUF

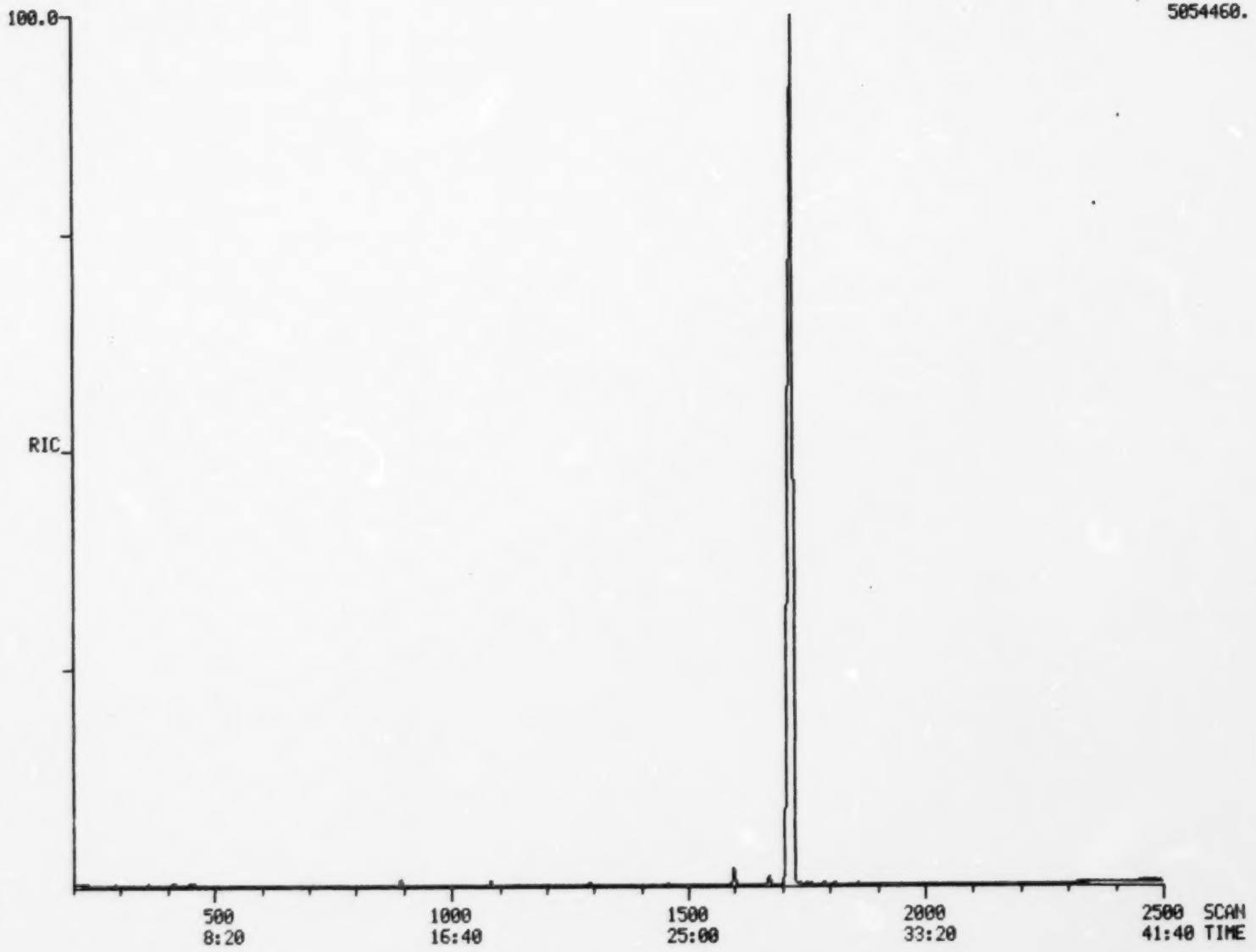

Figure 1. The total ion chromatogram of PUF blank cleaned by the compression method.

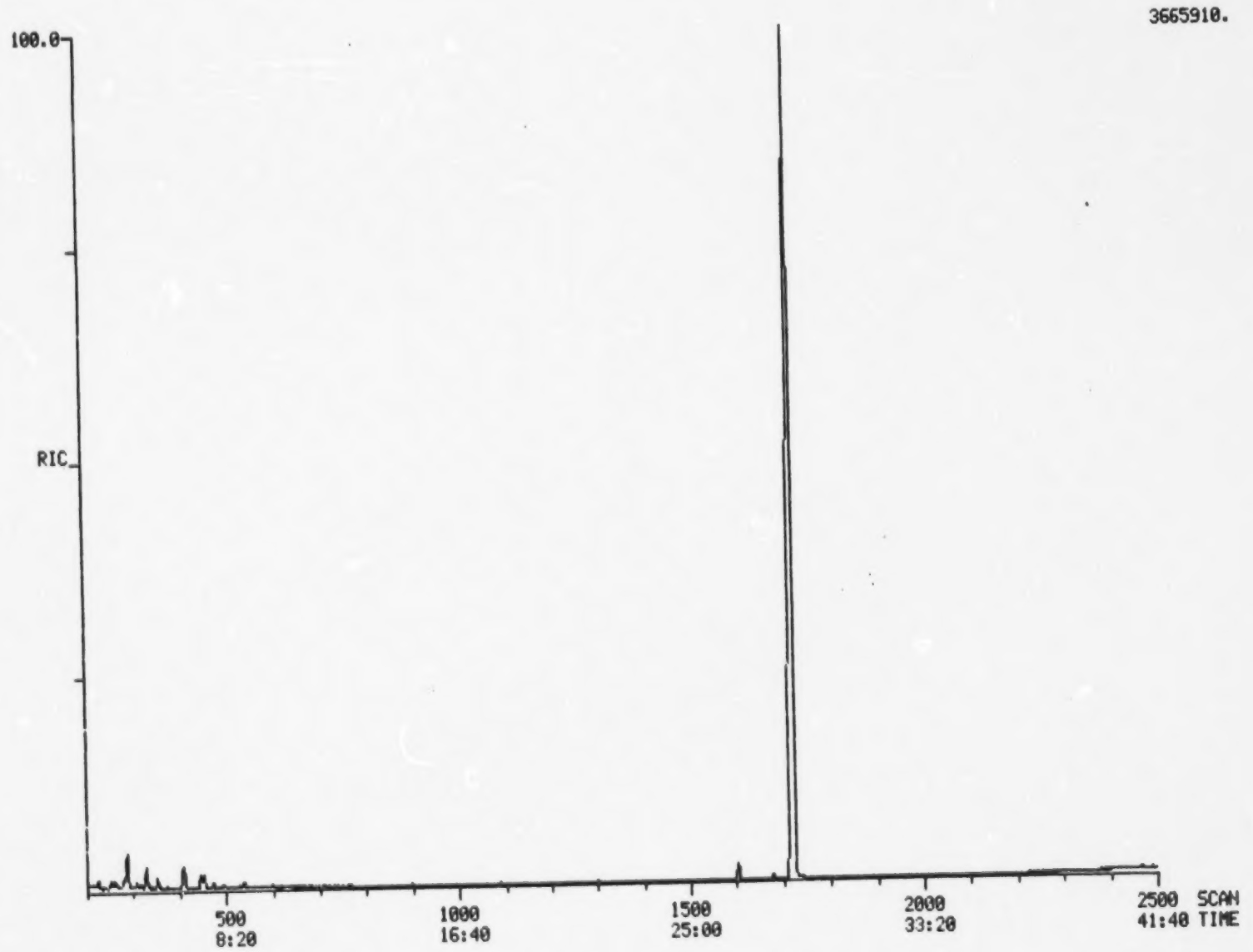

Figure 2. The total ion chromatogram of PUF blank cleaned by the combined compression and Soxhlet extraction method.

cartridges, indicating that these compounds are predominantly retained on the filter.

TABLE 5.1. LEVELS OF PAHs IN PUF CARTRIDGES CLEANED BY TWO DIFFERENT METHODS

Compound	Method of Cleaning	
	Compression Method Total Mass/PUF Cartridge, µg	Compression followed by Soxhlet Extraction Method Total Mass/PUF Cartridge, µg
Naphthalene	0.07	0.10
Phenanthrene	--(1)	--
Anthracene	--	--
Fluoranthene	--	--
Pyrene	--	--
Benz(a)anthracene	--	--
Chrysene	--	--
Cyclopenta(c,d)pyrene	--	--
1-Nitropyrene	--	--
Benzo(e)pyrene	--	--
Benzo(a)pyrene	--	--
Benzo(g,h,i)perylene	--	--
Coronene	--	--

(1) Not detected.

TABLE 5.2 RECOVERIES OF PAHs FROM SPIKED PUF CARTRIDGES USING TWO EXTRACTION METHODS - COMPRESSION AND SOXHLET EXTRACTION

Compound Name	Soxhlet Extraction, % Recovery					Compression Method, % Recovery				
	No. 1	No. 2	No. 3	No. 4	Average Value	No. 1	No. 2	No. 3	No.4	Average Value
D_8-Naphthalene	0.83	0.69	0.41	2.86	1.20	0.70	0.58	1.16	0.67	0.78
D_{10}-Phenanthrene	92.62	91.20	73.21	84.14	85.29	83.56	81.12	89.33	86.57	85.14
D_{10}-Pyrene	107.62	101.13	104.18	103.79	104.18	113.62	105.91	108.13	99.90	106.89
D_{12}-Chrysene	106.57	102.42	102.89	93.60	101.37	111.65	106.56	102.32	92.17	103.18
D_{12}-Benzo(a)pyrene	92.18	87.53	99.15	103.90	95.69	103.08	96.19	93.76	90.40	95.86

TABLE 5.3. LEVELS OF PAHs IN PUF CARTRIDGES EXTRACTED BY TWO METHODS - COMPRESSION AND SOXHLET EXTRACTION

Compound Name	Soxhlet Extraction, Total Mass, ng/m^3					Compression Method, Total Mass, ng/m^3				
	No. 1	No. 2	No. 3	No. 4	Average Value	No. 1	No. 2	No. 3	No.4	Average Value
Naphthalene	4.14	3.87	3.87	6.56	4.61	3.40	3.77	4.08	4.94	4.05
Phenanthrene	30.18	26.93	29.69	30.74	29.39	26.35	26.17	26.17	34.94	28.41
Anthracene	2.33	2.02	2.06	1.57	2.00	1.72	1.54	1.69	2.39	1.84
Fluoranthene	7.58	6.66	7.09	7.12	7.11	6.75	6.60	6.29	7.94	6.90
Pyrene	5.06	4.33	4.23	3.56	4.30	4.39	3.90	3.96	5.40	4.41
Benz(a)anthracene	--(1)	--	--	--	--	--	--	--	--	--
Chrysene	0.15	0.03	0.06	0.15	0.10	0.12	0.15	0.09	0.31	0.17
Cyclopenta(c,d)pyrene	--	--	--	--	--	--	--	--	--	--
1-Nitropyrene	--	--	--	--	--	--	--	--	--	--
Benzo(e)pyrene	--	--	--	--	--	--	--	--	--	--
Benzo(a)pyrene	--	--	--	--	--	--	--	--	--	--
Benzo(g,h,i)perylene	--	--	--	--	--	--	--	--	--	--
Coronene	--	--	--	--	--	--	--	--	--	--

(1) Not detected

The stability study was conducted to determine whether a significant loss of PAHs captured by PUF cartridges occurs during the storage period. Two sets of PUF samples were obtained for this study. The first set of PUF samples was stored at room temperature (~20°C) in the light, and the second set of samples was stored at room temperature in the dark. Average recoveries of the perdeuterated PAHs extracted from the PUF samples are given in Tables 5.4 and 5.5. Concentrations of native PAHs found in the PUF samples are calculated as ng/m^3 and are given in Tables 5.6 and 5.7.

Recoveries for the perdeuterated PAHs for the first set of PUF samples (stored in the light) ranged from 0.6 percent for D_8-naphthalene to 102.3 percent for D_{12}-Chrysene. Low recoveries were obtained for D_8-naphthalene, which decreased from 2.6 percent to 0.4 percent after 20 days storage. The low recovery and the decreasing recovery trend for D_8-naphthalene during storage are mainly due to the volatilization of this compound. The storage time does not appear to have adverse effects on the recoveries of D_{10}-phenanthrene, D_{10}-pyrene, and D_{12}-chrysene. The variations of recovery for these compounds were less than 15 percent and may be due to small variations in sampling and analysis procedures. It should be noted that the recoveries of D_{12}-benzo(a)pyrene decreased significantly with increased storage time:; the recoveries decreased from 92.1 percent to 11.7 percent after storage for 20 days. It is possible that oxidation or other degradation reactions of D_{12}-BaP may occur during storage.

In the second set of PUF samples (stored in the dark), the relative recovery data are similar to those obtained with the first set of samples. But the recovery of D_{12}-BaP decreased less in the second set of samples than in the first set. The recoveries decreased from 95.4 percent to 44.3 percent after 20 days storage. Even after 30 days, 29.5 percent of the D_{12}-BaP was recovered. It appears that the PUF-adsorbed D_{12}-BaP is more stable in the absence of light.

TABLE 5.4. RECOVERIES OF PAHs FROM PUF CARTRIDGES SPIKED PRIOR TO SAMPLING AS A FUNCTION OF STORAGE TIME. STORAGE CONDITIONS: 20°C, IN THE LIGHT

Compound Name	Percent Recovery Storage Time Between Sampling and Extraction, Days 1	10	20
D_8-Naphthalene	2.6(2.4,2.9)(1)	0.6(0.9,0.3)	0.4(0.4,0.4)
D_{10}-Phenanthrene	87.8(85.5,90.1)	90.8(87.2,93.4)	84.1(86.8,81.4)
D_{10}-Pyrene	98.6(95.7,101.5),	85.8(91.5,81.1)	91.4(88.4,94.4)
D_{12}-Chrysene	102.3(103.2,101.4)	88.8(86.1,91.5)	91.7(96.8,86.5)
D_{12}-Benzo(a)pyrene	92.1(94.6,89.6)	49.5(48.2,50.8)	11.7(12.1,11.3)

(1) The first number given is the mean of the duplicate samples; the second and third numbers are the range of the samples.

TABLE 5.5. RECOVERIES OF PAHs FROM PUF CARTRIDGES SPIKED PRIOR TO SAMPLING AS A FUNCTION OF STORAGE TIME. STORAGE CONDITIONS: 20°C, IN THE DARK

Compound Name	Percent Recovery Storage Time Between Sampling and Extraction, Days 1	10	20	30
D_8-Naphthalene	1.2(1.3,1.1)(1)	2.7(2.2,3.2)	1.1(0.8,1.4)	0.6(0.9,0.3)
D_{10}-Phenanthracene	88.3(86.9,89.7)	88.5(95.1,81.9)	84.5(87.2,81.8)	86.1(87.6,84.6)
D_{10}-Pyrene	97.6(100.1,95.1)	93.3(90.4,96.2)	87.1(80.4,93.8)	91.2(89.6,92.8)
D_{12}-Chrysene	100.0(97.2,102.8)	94.5(91.4,97.6)	101.1(103.9,98.3)	89.4(81.7,97.1)
D_{12}-Benzo(a)Pyrene	95.4(94.1,96.6)	51.9(49.8,56.0)	44.3(42.2,46.4)	29.5(27.2,31.8)

(1) The first number given is the mean of the duplicate samples; the second and third numbers are the range of the samples.

TABLE 5.6. LEVELS OF NATIVE PAHs FOUND IN PUF CARTRIDGES AS A FUNCTION OF STORAGE TIME. STORAGE CONDITIONS: 20°C, IN THE LIGHT

Compound Name	Concentration, ng/m3(1) Storage Time Between Sampling and Extraction, Days 1	10	20
Naphthalene	6.37(4.95,7.79)(2)	3.94(4.43,3.45)	2.95(2.73,3.17)
Phenanthrene	36.06(33.45,38.67)	29.41(26.80,32.02)	29.25(28.12,30.38)
Anthracene	0.61(0.71,0.51)	0.70(0.77,0.63)	0.41(0.38,0.44)
Fluoranthene	7.39(7.12,7.66)	6.33(5.78,6.88)	6.79(7.30,6.28)
Pyrene	5.46(5.43,5.49)	6.02(6.63,5.41)	5.84(6.04,5.64)
Benz(a)anthracene	0.22(0.16,0.28)	0.20(0.25,0.15)	0.23(0.34,0.12)
Chrysene	0.79(0.89,0.69)	0.66(0.69,0.63)	0.71(0.81,0.61)
Cyclopenta(c,d)pyrene	--(3)	--	--
1-Nitropyrene	--	--	--
Benzo(e)pyrene	--	--	--
Benzo(a)pyrene	--	--	--
Benzo(g,h,i)perylene	--	--	--
Coronene	--	--	--

(1) Expressed as ng per cubic meter of air sampled.

(2) The first number given is the mean of the duplicate samples; the second and third numbers are the range of the samples.

(3) Not detected

TABLE 5.7. LEVELS OF NATIVE PAHs FOUND IN PUF CARTRIDGES AS A FUNCTION OF STORAGE TIME. STORAGE CONDITIONS: 20°C, IN THE DARK

Compound Name	Concentration, ng/m^3(1) Storage Time Between Sampling and Extraction, Days 1	10	20	30
Naphthalene	9.80(9.41,10.19)(2)	9.04(9.43,8.65)	8.27(8.26,8.28)	6.17(6.47,5.87)
Phenanthrene	24.57(23.66,25.48)	29.72(32.96,26.48)	22.32(24.39,20.25)	29.38(29.91,28.85)
Anthracene	1.87(2.18,1.56)	0.95(1.01,0.89)	0.67(0.70,0.04)	1.01(1.04,0.98)
Fluoranthene	5.88(5.81,5.95)	6.03(6.52,5.53)	5.82(5.78,5.86)	6.61(6.54,6.68)
Pyrene	6.13(6.12,6.14)	6.68(6.60,6.76)	4.89(4.53,5.25)	5.56(5.95,5.17)
Benz(a)anthracene	0.18(0.19,0.17)	0.17(0.22,0.12)	0.09(0.12,0.06)	0.16(0.15,0.17)
Chrysene	0.19(0.18,0.19)	0.14(0.13,0.14)	0.20(0.15,0.25)	0.18(0.18,0.18)
Cyclopenta(c,d)pyrene	--(3)	--	--	--
1-Nitropyrene	--	--	--	--
Benzo(e)pyrene	--	--	--	--
Benzo(a)pyrene	--	--	--	--
Benzo(g,h,i)perylene	--	--	--	--
Coronene	--	--	--	--

(1) Expressed as ng per cubic meter of air sampled.
(2) The first number given is the mean of the duplicate samples; the second and third numbers are the range of the samples.
(3) Not detected.

Similar recovery trends were observed for the native PAHs. The storage time does not significantly affect the levels of phenanthrene, pyrene, and chrysene found in the PUF samples. Slightly decreasing concentrations were detected for naphthalene. Similar decreasing levels were observed for anthracene, an isomer of phenanthrene. The reactive PAH, cyclopenta(c,d)pyrene, higher-molecular weight PAHs ($\geq$252), and 1-nitropyrene were not detected in the PUF samples.

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